HYPERFINE STRUCTURE IN IONIZED BISMUTH

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A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

1931.

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(Received March 14, 1931)

Abstract

The hyperfine structure of several lines in the spectra of Bi II and Bi III have been determined. A method which facilitates the analysis of partially resolved line patterns is described. The level separations obtained from the analysis are compared with theoretical formulas showing the inadequacy of the present theory for the interaction of external electrons with nuclear spin.

Experimental

THE twenty-one foot eighty thousand line concave grating mounted in the third basement of the laboratory was used in this work. We have used the grating in Paschen mounting with the slit at fifty degrees from the normal. In the third, fourth and fifth orders, where we have worked, linear dispersions range from 0.47 to 0.87 Ångströms per millimeter and the practical resolving power is near two hundred thousand. Although the grating shows faint Rowland ghosts this is no limitation to fine-structure work, since these ghosts always lie far outside the fine-structure pattern. In extreme exposures a faint and diffuse line appears close on the short wave-length side of a sharp line. This false line causes little difficulty, however, since it appears only in over exposure and then at a fixed distance from the parent line. Although no attempt was made at temperature control the temperature of the spectrograph room was so constant that no appreciable broadening appeared after a twenty-four hour exposure.

Since the effect of fields and pressures in broadening spectral lines is considerable for ordinary light sources, special precautions attempting to avoid these influences are necessary in hyperfine structure work. Back has employed his vacuum arc most successfully in his work in arc spectra. Schüler[1] suggests the use of a modified form of the Paschen hollow cathode tube operating at liquid air temperatures. This type of source has been used by White and Ritchl[2] as well as by Schüler himself.

We have used an arc between a bismuth and a tungsten electrode in hydrogen at a few centimeters pressure in making a preliminary survey of the spectrum. This source gave several of the Bi II lines with fair sharpness. Later we used a metal discharge tube similar to that described by Schüler. Our only modification of Schüler's tube is the use of a removable molybdenum cylinder as hollow cathode. This molybdenum cathode has the advantage of contributing practically no lines to the spectrum and of being cleaned of im-

[1] H. Schüler, Zeits. f. Physik **56**, 149 (1930).
[2] H. E. White and R. Ritchl, Phys. Rev. **35**, 1146 (1930).

purities quickly. The bismuth was excited in helium, the metallic bismuth being placed inside the molybdenum cathode. The tube was operated in a water bath since lower temperatures were found to be of no advantage in the case of bismuth. In the discharge the lines of Bi I and Bi II appeared with nearly equal intensity while those of Bi III were somewhat less intense. An exposure of twenty-four hours was necessary in order to obtain some of the lines in the higher orders.

Analysis

The theory concerning hyperfine structure term separations predicts that hyperfine multiplets will follow the interval rule very accurately. Also the formulas for the line intensities in hyperfine line multiplets, which Hill[3] has derived by means of the quantum mechanics, should hold with accuracy. The fact that the interval and intensity rules can be relied upon enables one to construct graphs which aid greatly in the analysis of hyperfine line patterns. An observed line pattern is seldom completely resolved due to small separation in one or the other of the hyperfine multiplets giving rise to the line. The graphs are of particular use in the cases of imperfectly resolved line patterns.

Fig. 1a shows such a graph representing the possible line patterns in the case of a transition between two sets of levels in Bi II, each with a total extra-nuclear angular momentum of one quantum unit ($J=1$). Since the nuclear angular momentum quantum number of bismuth has been shown by Goudsmit and Back[4] to be $4\frac{1}{2}$, the resulting hyperfine multiplets should both be triple with fine quantum numbers of $3\frac{1}{2}$, $4\frac{1}{2}$, and $5\frac{1}{2}$. According to the interval rule the level separations should be $4\frac{1}{2}A$ and $5\frac{1}{2}A$, where A is called the separation factor. The distribution of the lines in the figure at any particular horizontal level gives a possible line pattern. The vertical coordinate, denoted by μ, is the ratio between the separation factors of the initial and final states. If B is the separation factor of the initial and A of the final hyperfine multiplet, $\mu=B/A$. The horizontal coordinate may be read in units of wave length or frequency as one chooses. Thus on the axis, $\mu=0$, we have a line pattern corresponding to the case of no separation of the initial levels, that is, a line triplet with the separations of the final multiplet, the separation ratio being $4\frac{1}{2}:5\frac{1}{2}$ as the interval rule requires. Positions a little above this axis, $\mu=0$, give line patterns due to slight separation of the initial levels as compared with the final levels. As we proceed to larger μ the graph represents the change in line pattern resulting from larger separations of the initial levels. The whole region above the axis (μ positive) gives patterns for cases in which both multiplets are regular or both inverted. Positions below this axis (μ negative) give patterns for cases in which one of the multiplets is inverted with respect to the other. The intensities of the lines are calculated from the formulas of Hill and the widths of the lines made roughly proportional to the expected intensities.

Fig. 1b gives a six-fold enlargement of the line $\lambda 5270$ of Bi II. It may be

[3] E. L. Hill, Proc. Nat. Acad. Sci. **15**, 779 (1929).
[4] S. Goudsmit and E. Back, Zeits. f. Physik **43**, 321 (1927).

observed that the line fits the graph precisely at $\mu = -0.261$. Because of its small intensity the line in the center of the figure does not appear on the photographic plate. The separations of the two multiplets giving rise to the line may here be read directly from the measured line separations.

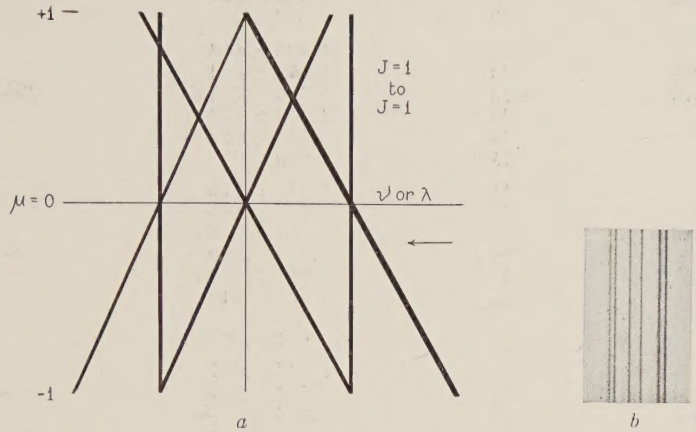

Fig. 1. Diagram for transition $J=1$ to $J=1$ compared with Bi II λ5270. $\mu = -0.261$, total $\Delta\nu = 4.93$ cm^{-1}. The arrow indicates where the line pattern fits the diagram.

The graphs are of greatest assistance in cases in which the observed line patterns are imperfectly resolved.[5] In such cases the level separations may be found if μ can be determined by comparing the observed pattern to the graph and one or two separations measured to give the scale. Fig. 2a gives

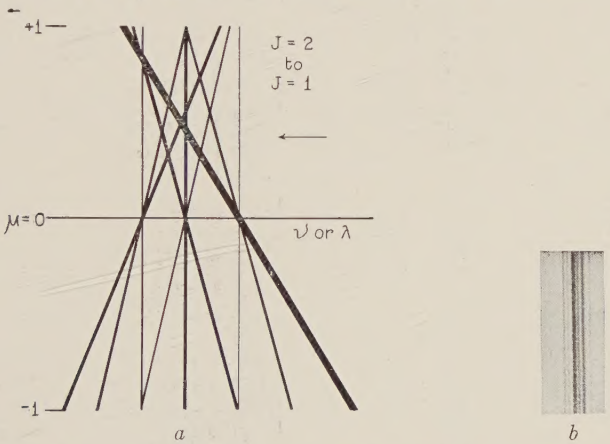

Fig. 2. Diagram for transition $J=2$ to $J=1$ compared with Bi II λ4705. $\mu = +0.457$ total $\Delta\nu = 2.71$ cm^{-1}. The arrow indicates where the line pattern fits the diagram.

the graph for the transition $J=2$ to $J=1$. Fig. 2b gives an example of a partially unresolved and poorly defined line pattern which may be analyzed by means of the graph. The pattern is a six-fold enlargement of the unclassified line λ4705 of Bi II as it appeared in the fourth order. It is found that this line

[5] Similar graphs applicable to Zeeman effect analysis are being prepared for publication

TABLE I. *Hyperfine structure of Bi II lines.*

λ ν	Intensity of components	Δν cm^{-1}	Combination
5719	40	3.895 ± .006	$2_1^0 - 7_0$
17480	50	2.140 ± .006	
	60	.000	
	20	4.926 ± .004	
5270	20	3.995 ± .004	
18970	20	3.166 ± .004	$2_1^0 - 8_1$
	20	2.149 ± .004	
	23	.553 ± .006	
	25	.000	
	15	3.215 ± .006	
5209	30	2.667 ± .006	
19192	60	2.166 ± .006	
	30	1.471 ± .009	$2_1^0 - 9_2$
	15	.964 ± .012	
	80	.783 ± .012	
	30	.000	
	8	− .694 ± .009	
	15	1.027 ± .007	
5144	20	.564 ± .007	$1_0^0 - 8_1$
19435	30	.000	
	5	1.850 ± .006	
5124	7	1.505 ± .009	
19510	10	1.105 ± .009	$9_2^0 - 16_1$
	14	.585 ± .006	
	18	.000	
	1	2.32 ± .02	
5091	2	1.83 ± .02	
19637	2	1.34 ± .03	$9_2^0 - 17_1$
	1	1.11 ± .03	
	3	.74 ± .03	
	1	.56 ± .03	
	5	.00	
	20	1.325 ± .007	
4994	5	1.071 ± .007	
20018	10	.734 ± .007	$10_1^0 - 19_2$
	8	.546 ± .007	
	10	.000	
	4	1.54 ± .03	
4730	10	1.35 ± .02	
21136	12	.99 ± .01	$9_2^0 - 19_2$
	12	.68 ± .01	
	6	.46 ± .02	
	6	.24 ± .02	
	15	.00	
	2	− .25 ± .02	
	7	2.058 ± .005	
4705	25	1.500 ± .005	
21248	10	1.017 ± .005	Unclassified
	30	.786 ± .003	
	8	.326 ± .008	
	12	.000	
	4	− .652 ± .005	
	3	3.53 ± .02	
4477	3	3.14 ± .02	
22330	3	2.33 ± .03	Unclassified
	3	1.50 ± .02	
	4	.49 ± .02	
	4	.00	

TABLE I (*Continued*)

λ / ν	Intensity of Components	$\Delta\nu$ cm^{-1}	Combination
	6	.64 ±.02	
4392	6	.30 ±.01	unclassified
22762	3	.00	
	10	2.62 ±.01	
4301	14	2.17 ±.01	
23244	6	1.70 ±.01	$7_2^0-12_3$
	12	1.52 ±.01	
	5	1.03 ±.01	
	18	.81 ±.01	
	5	.295±.005	
	24	.000	
	20	1.52 ±.01	
4079	15	.69 ±.01	
24509	10	.00	$6_1^0-10_2$
	7	1.45 ±.02	
3864	5	.66 ±.03	
25873	3	.00	$6_1^0-15_1$
	1	2.69 ±.04	
3846	2	2.14 ±.03	
25994	3	1.55 ±.02	$5_2^0-10_2$
	4	.88 ±.02	
	5	.00	
	4	3.21 ±.02	
3816	7	2.65 ±.01	
26198	15*	1.96 ±.01	$5_2^0-12_3$
	2	1.23 ±.02	
	10	1.00 ±.01	
	2	.27 ±.01	
	12	.00	
	2	1.65 ±.02	
3811	3	1.31 ±.02	
26232	5	.89 ±.01	$7_2^0-16_3$
	7	.47 ±.01	
	9	.00	
	6	1.25 ±.02	
3792	18	1.07 ±.02	
26364	22	.76 ±.01	$5_2^0-13_3$
	30	.41 ±.01	
	3	.00	
	20	8.84 ±.02	
3430	30	7.30 ±.03	
29146	40	5.29 ±.03	$4_2^0-12_3$
	50	2.88 ±.03	
	60	.00	
	1	8.2	
3111†	2	6.7	
32135	3	4.8	$4_2^0-16_3$
	4	2.7	
	5	.0	
	16	7.5	
2368†	12	5.1	
42217	10	3.0	$4_2-4_2^0$
	9	1.4	
	8	.0	

* An iron line coincides with this component giving the abnormal intensity.
† From the measurements of McLennan, McLay and Crawford.

pattern fits the graph with exactness at $\mu = 0.457$. The very faint component to the extreme right, which may not appear in the reproduction, is present on the original plate.

TABLE II. *Hyperfine structure of Bi III lines.*

λ ν	Intensity of Components	Δν cm^{-1}	Combination
	1	9.3 ±.3	
4750	2	8.1 ±.3	
21046	3	6.6 ±.3	$3_{2\frac{1}{2}} - 5f\,^2F_{2\frac{1}{2}}{}^0$
	4	4.7 ±.2	
	5	2.6 ±.1	
	6	.0	
	20	2.88 ± .01	
4561	5	2.36 ± .01	
21919	10	.52 ± .01	$7s^2S_{\frac{1}{2}} - 7p\,^2P_{\frac{1}{2}}{}^0$
	20	.00	
3695	10	2.16 ± .03	
27056	15	.00	$7s^2S_{\frac{1}{2}} - 7p\,^2P_{1\frac{1}{2}}{}^0$
	2	12.3	
3039†	3	10.7	
32896	4	8.9	$2_{2\frac{1}{2}} - 7p\,^2P_{1\frac{1}{2}}{}^0$
	5	6.6	
	7	3.6	
	9	.0	
	2	7.1	
2944†	3	5.4	
33957	4	3.0	$1_{1\frac{1}{2}} - 7p\,^2P_{\frac{1}{2}}{}^0$
	6	.0	
	1	9.3	
2184†	1	8.0	
45733	1	6.6	$3_{2\frac{1}{2}} - 6f\,^2F_{3\frac{1}{2}}{}^0$
	2	4.9	
	2	2.8	
	3	.0	

† From the measurements of McLennan, McLay and Crawford.

Tables I and II give the measurements on the line patterns of Bi II and Bi III, respectively, in terms of frequency differences. The line of the pattern from which the frequency differences are measured is in general the one of lowest frequency. In the few cases in which the line of lowest frequency is faint or unsuitable for other reasons another line has been selected. The method of measurement was such that the uncertainty in frequency difference between any two components of a pattern is not greater than the larger uncertainty following one of them, i.e., the uncertainties do not add. In the tables we give the wave-lengths to four significant figures only, since the patterns are broad and we have not made precise wave-length measurements.

We have been aided greatly in the hyperfine structure analysis by a paper recently published by McLennan, McLay and Crawford[6] in which they give the term analysis for Bi II and for Bi III and a few very wide hyperfine-structure measurements. We have included their measurements in our tables as those indicated by the symbol †.

[6] J. C. McLennan, A. B McLay and M. F. Crawford, Proc. Roy. Soc. **A129**, 579 (1930).

TABLE III. *Bi II level separations.*

Term value	Configuration*	Term designation	Total separation cm^{-1}	Separation factor
69126	$6p_{\frac{1}{2}}7s$	$1_0{}^0$	—	
69590	$6p_{\frac{1}{2}}7s$	$2_1{}^0$	3.91 ± 0.01	0.391
76143	$6s6p^3$	$4_2{}^0$	8.2 ± 0.2	0.41
79083	$6p_{\frac{1}{2}}6d_{1\frac{1}{2}}$	$5_2{}^0$	2.55 ± 0.10	0.127
80569	$6p_{\frac{1}{2}}6d_{1\frac{1}{2}}$	$6_1{}^0$	-1.65 ± 0.05	−0.165
82041	$6p_{\frac{1}{2}}6d_{2\frac{1}{2}}$	$7_2{}^0$	1.98 ± 0.15	0.099
88763	$6p_{1\frac{1}{2}}7s$	$9_2{}^0$	2.18 ± 0.10	0.109
89877	$6p_{1\frac{1}{2}}7s$	$10_1{}^0$	-0.53 ± 0.03	−0.053
88559	$6p_{\frac{1}{2}}7p_{1\frac{1}{2}}$	8_1	1.02 ± 0.01	−0.102
88781	$6p_{\frac{1}{2}}7p_{1\frac{1}{2}}$	9_2	2.50 ± 0.03	0.125
105077	$6p_{\frac{1}{2}}5f_{2\frac{1}{2}}$	10_2	-0.16 ± 0.06	−0.008
105281	$6p_{\frac{1}{2}}5f_{2\frac{1}{2}}$	12_3	-0.70 ± 0.15	−0.023
105443	$6p_{\frac{1}{2}}5f_{3\frac{1}{2}}$	13_3	1.95 ± 0.20	0.065
106441	$6p_{1\frac{1}{2}}7p_{\frac{1}{2}}$	15_1	-0.36 ± 0.08	−0.036
108272	$6p_{1\frac{1}{2}}7p_{1\frac{1}{2}}$	16_2	0.37 ± 0.15	0.012
108398	$6p_{\frac{1}{2}}8p_{\frac{1}{2}}$	17_1	-0.14 ± 0.10	−0.014
109897	$6p_{1\frac{1}{2}}7p_{1\frac{1}{2}}$	19_2	0.78 ± 0.04	0.039

* The configurations and term values are as given by McLennan, McLay and Crawford.

TABLE IV. *Bi III level separations.*

Term value	Configuration	Term designation	Total separation cm^{-1}	Separation factor
123143	$6s6p^2$	$1_{1\frac{1}{2}}$	7.5 ± 0.8	0.50
116943	$6s6p^2$	$2_{2\frac{1}{2}}$	12.5 ± 0.8	0.50
111105	$7s$	$^2S_{\frac{1}{2}}$	2.36 ± 0.01	0.472
89765	$6s6p^2$	$3_{2\frac{1}{2}}$	9.3 ± 0.6	0.37
89188	$7p$	$^2P_{\frac{1}{2}}{}^0$	0.52 ± 0.01	0.104
84053	$7p$	$^2P_{1\frac{1}{2}}{}^0$	0.31 ± 0.05	0.021

Tables III and IV give the level separations as determined from our measured line patterns with the aid of the graphs. In the tables we have used the term designation as given by McLennan, McLay and Crawford. In all cases we give the total hyperfine-multiplet separation. Negative separation in the table indicates inversion of the multiplet. Although the individual level separations could usually be determined, the uncertainty was in most cases too large for the data to be a valuable test of the interval rule. The separations of two of the multiplets of bismuth II are determined with a higher degree of accuracy. They are:

Term	Total separation	Individual separations	
$2_1{}^0$	$3.91 \pm .01$	$2.15 \pm .01$	$1.76 \pm .01$
8_1	$-1.02 \pm .01$	$-.56 \pm .01$	$-.46 \pm .01$

We may say that the interval rule is obeyed to within the limit of observational uncertainty in all cases. We believe that the estimates of uncertainty given in the tables are extremely liberal.

It is evident that the hyperfine structure analysis serves to verify much of the term assignment of McLennan, McLay and Crawford from the fact that we are able to use their term designation. We find, however, no evidence of the existence of the tentative term denoted by them as 3°.

We have been able to measure the structure of three lines which without doubt belong to Bi II but which have not been classified by McLennan, McLay and Crawford. We make no attempt to classify these lines in the general term system but do give the hyperfine separations of the levels from which they originate. Two possibilities arise in such cases since there is no way of deciding which level is initial. These lines and the level separations derived from them are as follows:

Wave-length of line	Total separation of initial levels	Total separation of final levels
4705	2.48 ± 0.05 $(J=2)$	2.71 ± 0.01 $(J=1)$
	or	
	-2.71 ± 0.01 $(J=1)$	-2.48 ± 0.05 $(J=2)$
4477	-0.85 ± 0.04 $(J=2)$	2.68 ± 0.04 $(J=2)$
	or	
	-2.68 ± 0.04 $(J=2)$	0.85 ± 0.04 $(J=2)$
4392	0.60 ± 0.15 $(J=1)$	small $(J=0?)$
	or	
	small $(J=0?)$	-0.60 ± 0.15 $(J=1)$

Theoretical Discussion

In a previous[7] paper one of us has given formulas for the hyperfine-structure separations for different states of the same atom. In that paper it was already pointed out that the theoretical results were in disagreement with the experimental data, even in the simple case of a one-electron spectrum. We now wish to discuss our material in Bi II and Bi III together with the known data for Bi I[8] in the light of these theoretical expressions.

Bismuth I. The normal state, $6p^3$, does not yet show extreme (j,j) coupling. We may, however, apply the formulas derived on the assumption of extreme (j,j) coupling to the two levels with $J=2\frac{1}{2}$ and $J=\frac{1}{2}$, respectively, since these two quantum numbers occur only once in this configuration and the hyperfine separations of the levels are therefore independent of the type of coupling. The individual electrons of the configuration are considered as acting separately except for their screening effect upon one another. Thus the separation factor of a hyperfine multiplet is expressible in terms of separation factors for the electronic states. These considerations are similar to those used in the treatment of ordinary multiplet separations. The following table gives the observed separation factors for several states together with the formulas[9] applying both in case of (j,j) coupling and of Russell-Saunders coupling.

[7] S. Goudsmit, Phys. Rev. **37**, 663 (1931).

[8] P. Zeeman, E. Back and S. Goudsmit, Zeits. f. Physik **66**, 1 (1931).

[9] For all following formulas see S. Goudsmit, Phys. Rev. **37**, 663 (1931).

Term	Observed separation factor	Formula	
		(j,j) coupling	Russell-Saunders coupling
$6p^3\ {}^4S_{1\frac{1}{2}}$	~ -0.005	a'	0
$^2D_{1\frac{1}{2}}$	-0.040	$1\frac{1}{5}a'-\frac{1}{5}a''$	$^{16}/_{25}a$
$^2D_{2\frac{1}{2}}$	0.081	$\frac{4}{5}a'+\frac{1}{5}a''$	$^{24}/_{25}a$
$^2P_{\frac{1}{2}}$	0.375	a''	$2\frac{2}{3}a$

In (j,j) coupling the separation factor for the $6p_{1\frac{1}{2}}$ electron is denoted by a' and that for the $6p_{\frac{1}{2}}$ electron by a''. In Russell-Saunders coupling it has no meaning to distinguish between the $6p_{\frac{1}{2}}$ and the $6p_{1\frac{1}{2}}$ states so one can only express the separation factor in terms of the common quantity, a. The quantities a' and a'' are not independent, for, according to the theory, one has the relations,

$$a' = \frac{8}{15}a \text{ and } a'' = \frac{8}{3}a, \text{ thus } a' = \frac{1}{5}a''.$$

The experimental data are not at all in agreement with these results. The last two states in the table, for which the formulas ought to hold, regardless of the type of coupling, show clearly that a' is much smaller than $1/5a''$. One finds from these two levels

$$a' = 0.008$$
$$a'' = 0.375.$$

These values do not agree exactly with those obtained from the first two levels of the table, but this may be ascribed to the deviation from the extreme (j,j) coupling. It is certainly significant that the $^2D_{1\frac{1}{2}}$ level shows a negative separation factor again indicating that a' is too small.

The next configuration of interest is $6p^27s$. The assignment of electron configuration in this case is not quite certain as this configuration is mixed with the $6p^26d$ levels. This also may cause large second order corrections which make our formulas invalid. The observed data for this configuration, which is near extreme (j,j) coupling, together with the formulas applying in (j,j) coupling are as follows:

Term	Observed separation factor	Formula (j,j) coupling
$6p^27s\ 1_{\frac{1}{2}}$	0.166	c
$4_{1\frac{1}{2}}$	~ 0	$\frac{5}{6}a'-\frac{1}{6}a''+\frac{1}{3}c$
$5_{\frac{1}{2}}$	-0.142	$1\frac{2}{3}a'-\frac{1}{3}a''-\frac{1}{3}c$
$7_{2\frac{1}{2}}$	0.127	$\frac{3}{5}a'+\frac{1}{5}a''+\frac{1}{5}c$
$8_{1\frac{1}{2}}$	0.094	$^9/_{10}a'+^3/_{10}a''-\frac{1}{5}c$

Here the separation factor of the $7s$ electron is denoted by c. In this example the first level lies isolated from the others, hence one expects the formula to hold. The other levels form a group in which levels with $J=\frac{1}{2}$ and $J=2\frac{1}{2}$ occur only once. For these two levels the formulas ought also to be correct. From these one obtains:

$$c = 0.166$$
$$a' = 0.026$$
$$a'' = 0.390.$$

These values are in fair agreement with the data for the two observed levels with $J = 1\frac{1}{2}$. The value of a'' is in good agreement with what we obtain from the p^3 configuration. The value of a' agrees only in order of magnitude. However, we may not rely too much upon this value since it is so small that it may be much influenced by inaccuracy in the data as well as by second order corrections to our formulas. The significant point is that we again find a' to be much smaller than $1/5a''$.

Bismuth II. For the configuration $6p\ 7s$ we have extreme (j,j) coupling. The formulas and observed data for this case are:

Term	Observed separation factor	Formula (j,j) coupling
$6p_{\frac{1}{2}}7s\ 2_1{}^0$	0.391	$\frac{1}{2}a''+\frac{1}{2}c$
$6p_{1\frac{1}{2}}7s\ 9_2{}^0$	0.109	$\frac{3}{4}a'+\frac{1}{4}c$
$10_1{}^0$	−0.053	$1\frac{1}{4}a'-\frac{1}{4}c$

We expect the values of a', a'' and c to be somewhat larger than in Bi I because the screening has decreased. This will have the greatest influence upon the outer $7s$ electron and therefore upon c. We find

$$a' = 0.028$$
$$a'' = 0.430$$
$$c = 0.352$$

These values are in good agreement with our expectation.

For other configurations, such as $6p\ 6d$ and $6p\ 7p$, we expect only qualitative agreement, as the separation factors for the $6d$ and $7p$ are probably smaller than the errors due to second order corrections to our formulas and errors in our measurements. In the case of the $6p\ 6d$ configuration we have:

Term	Observed separation factor	Formula (j,j) coupling
$6p_{\frac{1}{2}}6d_{1\frac{1}{2}}\ 5_2{}^0$	0.127	$\frac{1}{4}a''+\frac{3}{4}d''$
$6_1{}^0$	−0.165	$-\frac{1}{4}a''+1\frac{1}{4}d''$
$6p_{\frac{1}{2}}6d_{2\frac{1}{2}}\ 7_2{}^0$	0.099	$-\frac{1}{6}a''+1\frac{1}{6}d'$

Here the symbols d' and d'' denote the separation factors of the $6d_{2\frac{1}{2}}$ and $6d_{1\frac{1}{2}}$ electrons, respectively. The first two states give:

$$a'' = 0.565$$
$$d'' = -0.019$$

It is strange to find a small negative value for d'', but we do not know that this value is entirely reliable. The experiment result for $7_2{}^\circ$ would give a very large value for d', which is even less understandable. Perhaps the assignment of the configuration is incorrect for this level.

As examples of the $6p\ 7p$ configuration we have:

Term	Observed separation factor	Formula (j,j) coupling
$6p_{\frac{1}{2}}7p_{1\frac{1}{2}}\ 8_1$	-0.101	$-\frac{1}{4}a''+1\frac{1}{4}e'$
9_2	0.125	$\frac{1}{4}a''+\frac{3}{4}e'$

Here e' denotes the separation factor for the $7p_{1\frac{1}{2}}$ state. We find:

$$e' = 0.012$$
$$a'' = 0.464.$$

Again a'' is in good agreement with what we expect.

For the $6p\ 5f$ configuration we have:

Term	Observed separation factor	Formula (j,j) coupling
$6p_{\frac{1}{2}}5f_{2\frac{1}{2}}\ 10_2$	-0.008	$-\frac{1}{6}a''+1\frac{1}{6}f''$
12_3	-0.023	$\frac{1}{6}a''+\frac{5}{6}f''$
$6p_{\frac{1}{2}}5f_{3\frac{1}{2}}\ 13_3$	0.065	$-\frac{1}{8}a''+1\frac{1}{8}f'$

Here f'' denotes the separation factor of the $5f_{2\frac{1}{2}}$ electron and f' that of the $5f_{3\frac{1}{2}}$ electron. These data give no sensible result. Perhaps the assignment of configuration is incorrect, or it may be that there are large second order effects due to the proximity of these levels to other even levels.

Bismuth III. The interesting configuration here is $6s\ 6p^2$. The hyperfine structure is known for three of the levels. For extreme (j,j) coupling, which may not be quite correct here, we have:

Term	Observed separation factor	Formula (j,j) coupling
$6s\ 6p^2\ 1_{1\frac{1}{2}}$	0.50	$\frac{5}{6}a'-\frac{1}{6}a''+\frac{1}{2}b$
$2_{2\frac{1}{2}}$	0.50	$\frac{3}{5}a'+\frac{1}{5}a''+\frac{1}{5}b$
$3_{2\frac{1}{2}}$	0.37	$\frac{4}{5}a'+\frac{1}{5}b$

The separation factor of the $6s$ electron is here denoted by b. The above data give us:

$$a'' = 0.66$$
$$a' = 0.01$$
$$b = 1.80.$$

Due to the fact that the screening is here much less than in the previous cases we find a'' to be larger than before. We cannot, of course, be sure that the value found is just the one expected without making complicated calculations as to screening effects. The value of a' is smaller than the uncertainty in measurement and therefore not reliable.

For the $7s$ configuration we find:

Term	Observed separation factor	Formula* (j,j) coupling)
$7s\ ^2S_{\frac{1}{2}}$	0.472	c

Comparing this value of c with the previous values we find the expected large increase. The experimental values for c are, Bi I:0.166; Bi II:0.352; Bi III:0.472.

We can make a similar comparison of the separations due to the $6s$ electron. The large hyperfine structure of the far ultraviolet lines $\lambda 864$ and $\lambda 1139$ observed by Arvidson[10] is probably that of the $6s$ state of Bi V. Furthermore, one level of the $6s\ 6p^3$ configuration of Bi II is at present known. Assuming (j,j) coupling one obtains:

Term	Observed separation factor	Formula (j, j) coupling
Bi II $6s6p^3\ 4_2{}^0$	0.41	$\frac{3}{4}a' + \frac{1}{4}b$
Bi V $6s$	2.6	b

Since a' is of the order of 0.01 this gives $b = 1.60$ for Bi II. Comparing the different values for b, we find, Bi II: 1.60; Bi III: 1.80; Bi V: 2.6.

Conclusions

The above discussion shows that in some respects the experimental results obey the theoretical formulas whereas in others there is distinct disagreement. It is possible to determine in more detail where the discrepancy lies. The formulas as they are given here in terms of a' and a'' explicitly are more or less independent of the type of interaction which causes the hyperfine splitting. One takes a given interaction for a definite state of a single electron and calculates by means of well-known methods the result when this electron is not alone but part of a more complicated configuration. Such formulas are based upon well-known quantum mechanical rules and can in many cases be derived by simple methods using the vector model. Similar ones have been shown to hold for multiplet separations, g-values, etc. It is therefore not surprising that the formulas are also valid here, for if they were not it would mean that ordinary perturbation theory could not be applied to our problem.

The discrepancy was found, however, in the relation between a' and a'',

$$a' = \frac{1}{5} a''.$$

Everywhere we find a' much too small. This relation, however, can be obtained only by considering in detail the interaction between the nuclear spin and the orbital and spin magnetism of the external electrons.[11] It is on this point that the present theory seems to be incorrect. We hope that the material gathered here may prove useful as a guide for the improvement of the quantum mechanics of spin-spin interaction.

[10] G. Arvidson, Nature **126**, 565 (1930).

[11] Compare S. Goudsmit, Phys. Rev. **37**, 663 (1931).